



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| <b>(54) Title:</b> PROCESS AND LOW SODIUM CATALYST FOR THE PRODUCTION OF FORMALDEHYDE FROM METHANE<br><br><b>(57) Abstract</b><br><br>Formaldehyde is made from methane (such as from natural gas) and a molecular oxygen containing gas by using a silica supported catalyst having less than 350 parts per million by weight of sodium and having a catalytically effective amount of MoO <sub>3</sub> . The low sodium form of the silica support can be made by washing silica gel or precipitated silica, by using a fumed silica or by making an ultrapure form of silica having a silica purity of at least 99.99% silica. The ultrapure form can be made by the hydrolysis of silicon tetraalkoxides. In general, the lower the sodium level, the better is the catalyst. |           |                                                                                                                                                                                                                                                                                                                                                                                     |

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- 1 -

PROCESS AND LOW SODIUM CATALYST FOR THE PRODUCTION OF  
FORMALDEHYDE FROM METHANE

Background of the Invention

1. Field of the Invention

This invention relates to a highly selective method of producing formaldehyde,  $\text{HCHO}$ , by the partial oxidation of methane using a special type of catalyst and to a unique, highly selective formaldehyde-forming catalyst.

2. Description of the Previously Published Art

The major commercial process to make formaldehyde is from methanol. This involves the steam reforming of methane with high grade heat to convert the methane into syn gas. The syn gas is reacted to form methanol while giving off low grade heat. Then the methanol is oxidized to formaldehyde while giving off additional low grade heat. This synthesis procedure requires multiple steps and it involves poor energy usage.

In the past a small fraction of formaldehyde was made by the partial oxidation of lower petroleum hydrocarbons which involved the partial oxidation of the hydrocarbon gas with air or oxygen under pressure, followed by rapid cooling, condensation, and absorption of the products in water to give a crude solution, which must then be refined to separate formaldehyde from the other reaction products, such as methanol, acetaldehyde, propyl alcohol, propionaldehyde, and

- 2 -

organic acids. Formaldehyde is isolated as a dilute solution, which must be concentrated to market strength. Propane and butane are the basic hydrocarbon raw materials for formaldehyde. Products manufactured by oxidation of propane and butane include formaldehyde, acetaldehyde, acetone, propionaldehyde, methanol, n-propyl alcohol, isopropyl alcohol, and butyl alcohols.

The German Offenlegungsschrift 2,404,738 to Bayer discloses oxidizing methane to formaldehyde by using many different types of metal oxides which may be placed on many different types of supports. The metal oxides are in Groups V, VI and/or VII of the Periodic Table. Among those listed are oxides of vanadium, niobium, tantalum, chromium, uranium, molybdenum, tungsten, manganese, technetium and rhenium, mixtures of these oxides with each other, and mixtures of these oxides with other oxides such as silica, alumina, iron oxide, calcium oxide, magnesia, sodium oxide or potassium oxide. In the first example using methane, the catalyst is 10 wt% Mo as  $\text{MoO}_3$  on silica.

This reference is not helpful in finding an optimum methane conversion catalyst. It provides no attention as to the criticality of the support. It groups silica with alumina and other metal oxides yet, as will be shown in the following examples, alumina when used as a support is not as effective as the catalyst of the present invention.

Furthermore the Bayer reference provides no attention to the criticality of having a low sodium

- 3 -

concentration. As will be shown in the following Comparison Example 1 and reported in Table 1, even when the Bayer molybdenum oxide-silica combination is used, as in Example 1 of the German patent application, the selectivity to formaldehyde is lower than that obtained with the present invention. This difference in result is believed due to the significant levels of sodium which can be present in silica. Sodium is present in most forms of silica that are synthesized in aqueous media because the conventional starting materials contain sodium. Offenlegungsschrift 2404738 goes so far as to specify that up to 5 wt%  $\text{Na}_2\text{O}$  may be present in the working catalyst. As will be shown in Examples 7-10, sodium in these concentrations has a profoundly deleterious effect on selectivity to formaldehyde in the partial oxidation of methane.

U. S. Patent No. 3,996,294, to Imre et al and assigned to Bayer discloses the use of a silica catalyst which does not contain any molybdenum to produce formaldehyde from methane. As will be shown in the examples, a catalyst consisting purely of silica, such as Cabosil (a product of Cabot Corporation), exhibits a lower selectivity to formaldehyde than is obtained with the catalyst of the present invention. Some of the examples in the Imre et al patent employ catalysts made substantially of silica along with small amounts of other metal oxides. There is no example given of using molybdenum oxide, although, as in the companion German Offenlegungsschrift, there is a broad list of metal oxides which can be used, including oxides of aluminum, iron, vanadium, molybdenum,

- 4 -

tungsten, calcium, magnesium, sodium or potassium with a specific reference that up to 5% of  $\text{Na}_2\text{O}$  can be used.

Japanese Patent Publication 58-92629 discloses a  $\text{SiO}_2\text{-MoO}_3$  catalyst, using  $\text{N}_2\text{O}$  or oxygen as oxidants. They report negligible selectivity to methanol or formaldehyde in the case of  $\text{O}_2$  oxidation. In the publication of Liu et al (J. Chem. Soc. Chem. Commun. 1982, 78 and J. Am. Chem. Soc, 1984, 106, 4117) a molybdena-silica catalyst is described, which also uses nitrous oxide for the partial oxidation of methane to formaldehyde and methanol. The use of  $\text{N}_2\text{O}$  as an oxidant is prohibitively expensive. Also, the silica in the catalyst is a fumed silica which is an expensive form of silica.

British Patent 1398385 discloses a methane partial oxidation catalyst consisting of  $\text{MoO}_3$  and  $\text{CuO}$  in the absence of carrier or binder. The inventors state, however, that the presence of at least 2 vol. % of a higher hydrocarbon must be present for the process to be effective, and their principal oxygenated product is methanol. Formaldehyde selectivity reaches a maximum of 15.5%

British Patent 1244001 discloses several catalysts for the partial oxidation of hydrocarbons. All of these catalysts contain  $\text{MoO}_3$ . The inventors claim that the principal oxygenated product is methanol, and the maximum selectivity to formaldehyde is 8%.

### 3. Objects of the Invention

It is an object of this invention to produce formaldehyde from methane without the production of a large number of by-products so as to avoid the

- 5 -

attendant separation problems and to obtain a catalyst which produces this result.

It is a further object of this invention to partially oxidize methane to form formaldehyde.

It is a further object of this invention to convert methane to formaldehyde with high selectivity.

It is a further object of this invention to obtain a methane conversion catalyst which converts methane to formaldehyde with high selectivity.

It is a further object of this invention to produce a methane conversion catalyst with a silica support having a low sodium concentration.

It is a further object of this invention to produce a methane conversion catalyst from economical and commercially available forms of silica which are treated to reduce the sodium content.

It is a further object of this invention to produce a methane conversion catalyst from an acid washed silica or an acid washed precipitated silica which has a low sodium level.

It is a further object of this invention to produce a methane conversion catalyst with an ultrapure silica support having a low sodium concentration.

It is a further object of this invention to produce a methane conversion catalyst having a selectivity of greater than 40% to the formation of formaldehyde when operating at an oxygen consumption value of 3.2%.

These and further objects will become apparent as the description of the invention proceeds.

- 6 -

Summary of the Invention

A catalytic process has been developed which converts methane to formaldehyde with high selectivity. It employs a catalyst which is made of molybdenum trioxide,  $\text{MoO}_3$ , supported on silicon dioxide (silica) containing low levels of sodium. The molybdenum trioxide is present in concentrations from a catalytically effective amount to 50 wt. % Mo, and especially preferred values are between about 0.5 wt. % and 15 wt. % Mo. Although higher  $\text{MoO}_3$  loadings such as greater than 15 wt. % Mo could be used, such catalysts rapidly lose  $\text{MoO}_3$  due to sublimation. Because this sublimation loss could have serious consequences on downstream processes, such high  $\text{MoO}_3$  loadings are not preferred. The silica support can have a surface area in the range of 20-1000  $\text{m}^2/\text{g}$ , and more preferably in the range of 30-600  $\text{m}^2/\text{g}$ . The silica support should contain a low amount of sodium such as in the range of between 0 and 350 ppm Na, preferably between 0 ppm and 100 ppm Na and most preferably between 0 and 20 ppm Na or at a level of 1 ppm or less. Commercially available and relatively inexpensive forms of silica such as silica gel or precipitated silica can be used and treated with an acid wash to remove the excess sodium.

A novel  $\text{MoO}_3$  containing catalyst which provides the highest selectivity for converting methane to formaldehyde utilizes an ultrapure silica support which has a silica content of at least 99.99 wt% silica and a sodium content of less than 50 ppm. More preferably forms have sodium contents of less than 4 ppm and more preferably less than 2 ppm. These catalysts provide



- 7 -

very high turnover numbers on the order of 38 micromoles of formaldehyde per square meter of catalyst per hour. Such a turnover rate is approximately 6 times higher than similar  $\text{MoO}_3$  loaded catalysts where the support is a fumed silica. Higher turnover numbers are advantageous, since they allow reactors to be reduced in size, with a consequent decrease in capital outlay.

#### Description of the Preferred Embodiments

The present invention discloses the ability to have methane converted to formaldehyde with a high selectivity by reacting methane simultaneously with a molecular oxygen containing gas when employing a catalyst having a catalytically effective amount of  $\text{MoO}_3$  on a silica support where the silica support is critically selected such that it has a sodium content of less than 350 ppm Na. As will be seen in the following examples, this encompasses a broad range of silica supports. Commercially available and relatively inexpensive forms of silica such as silica gel or precipitated silica can be used and treated with an acid wash to remove the excess sodium. Among the preferred silica supports is an ultrapure silica having a  $\text{SiO}_2$  content of at least 99.99 wt%. This silica can be prepared by the hydrolysis of a silicon tetraalkoxide. A catalyst made from this ultrapure support is shown to have the highest selectivity and the highest turnover numbers.

The catalyst can be prepared by either the incipient wetness technique or by evaporation to

- 8 -

dryness of a slurry of the low sodium form of silica in a molybdenum-containing solution. In the incipient wetness technique particles of silica are impregnated by an amount of a molybdenum-containing solution equal to the pore volume of the silica being impregnated. In the evaporation to dryness technique the particles of silica are placed in a volume of aqueous molybdenum-containing solution and the solvent evaporated.

If the catalyst is in a powder form, it can be pelleted, crushed and screened to obtain uniform size particles for loading into the reactor. The size of the particles can be adjusted and selected depending on the geometry of the reactor.

The preferred form of molybdenum for impregnation is ammonium paramolybdate, which dissolves in water or in a very dilute hydrogen peroxide solution. Other possible molybdenum salts would include molybdenum oxalate and possible phosphomolybdic acid.

The catalysts produced by either of these preferred methods have the molybdenum trioxide,  $\text{MoO}_3$ , present in concentrations between a catalytically effective amount which can be as low as 0.5 wt. % and 50 wt. % Mo, and especially preferred values are between 0.5 wt. % and 15 wt. % Mo. When catalysts are made with  $\text{MoO}_3$  loadings higher than about 15 wt. % Mo, the catalysts rapidly lose some of the  $\text{MoO}_3$  due to sublimation. These higher  $\text{MoO}_3$  loaded catalysts are not preferred because the sublimed  $\text{MoO}_3$  could travel to downstream processes where it would adversely affect these processes.

- 9 -

For the molybdenum trioxide-silica catalysts to be maximally selective for formaldehyde synthesis from methane, it appears the silica component must possess a low sodium level. This result may be achieved by using silica with an intrinsically low sodium level such as Cabosil, a product of Cabot Corporation, or by removing sodium from a form of silica with an intrinsically high sodium level such as Intermediate Density ("ID") Silica Gel or a precipitated silica such as Sylox-15. Both of these products are made by the Davison Chemical Division of W. R. Grace & Co. A further way to achieve the low sodium level is to use an ultrapure form of silica which has a  $\text{SiO}_2$  content of at least 99.99 wt. %. This can be made, for example, by the hydrolysis of a silicon tetraalkoxide.

The silica should ultimately have a sodium content in a range of between 0 and 350 ppm Na, preferably between 0 ppm and 100 ppm Na and most preferably between 0 and 20 ppm Na or at a level of 1 ppm or less. As will be illustrated in Examples 7-10, the presence of even small concentrations of sodium has a profoundly deleterious effect on the HCHO selectivity of methane oxidation, when it is catalyzed by the  $\text{MoO}_3\text{-SiO}_2$  system. The surface area of the silica is in the range of 20-1000  $\text{m}^2/\text{g}$ , preferably between 30  $\text{m}^2/\text{g}$  and 600  $\text{m}^2/\text{g}$ .

Although fumed silicas can have low sodium contents, acid washed silica gels and precipitated silicas have the significant advantage of being between one half and one third as expensive, mainly due to the far lower raw material costs involved.

- 10 -

The catalyst can be used to oxidize methane to formaldehyde at temperatures preferably between 500 and 700°C, a variety of pressures including atmospheric, space velocities between 1,000 and 20,000 hr<sup>-1</sup> (GHSV at NTP) and gas compositions from 0.5% O<sub>2</sub> (as oxygen or air) in CH<sub>4</sub> to the upper explosion limit which is dependent on pressure and concentration of inerts as discussed by C. M. Cooper and P. J. Weizevich, Ind. Eng. Chem., 21, (1929) 1210. Under optimal conditions, formaldehyde selectivities in excess of 90% (carbon basis) can be obtained.

The oxygen consumption value is determined as the difference between the inlet and outlet oxygen concentrations. When operating at oxygen consumption values of 3.2%, the catalysts made according to the present invention desirably have selectivities of greater than 40%.

The ultrapure silica support is preferably made by hydrolyzing an alcoholic solution of a silicon tetraalkoxide such as silicon tetraethoxide, followed by slow drying and calcination.

Having described the basic aspects of our invention, the following examples are given to illustrate specific embodiments thereof.

#### Example 1

This example illustrates the preparation of a catalyst using an ultrapure form of silica.

The ultrapure material was made by dissolving 104 g silicon tetraethoxide in 104 g ethanol. Concentrated ammonia solution was added to the mixture until the pH

- 11 -

exceeded 9.0. Gellation began to occur immediately, and the supernatant was allowed to evaporate overnight. The gel was dried at 70° for 5 days in air, followed by calcination at 500°C for 2 hours in air.

A catalyst was prepared by impregnating 5 g of the silica thus formed by incipient wetness with 0.158 g ammonium paramolybdate 4-hydrate and calcining at 482°C for three hours. The resulting catalyst had a molybdenum loading of 1.6 wt% and sodium level below the detection limit of inductively-coupled plasma analysis techniques. The BET surface area was 47 m<sup>2</sup>/g. The catalyst was pressed together, crushed and screened to US 25-35.

#### Example 2

This example illustrates the preparation of a catalyst using a fumed silica.

The catalyst was prepared by impregnating 50 g. of "Cabosil", a fumed silica made by Cabot Corp. with 10.82 g ammonium paramolybdate 4-hydrate by incipient wetness and calcining the impregnated product at 482°C for 3 hours. The resulting catalyst had a molybdenum loading of 9.75 wt.% and a sodium level lower than 4 ppm. The surface area was approximately 210 m<sup>2</sup>/g (BET). The catalyst was pressed together, crushed and screened to U. S. 25-35.

#### Example 3

This example illustrates the preparation of a catalyst using an acid washed silica gel.

A 15 g portion of dry Davison "ID" silica gel, which had previously been washed in dilute H<sub>2</sub>SO<sub>4</sub>

- 12 -

solution having a pH of 3 at 100°C for 2 days, was screened to US 25-35 and impregnated by immersion in a solution of 3.25 g ammonium paramolybdate 4-hydrate in 30 cc water, followed by evaporation to dryness and calcination at 600°C for 4 hours. The resulting catalyst had a surface area of 232 m<sup>2</sup>/g, a molybdenum loading of 8.63 wt.% and a sodium level less than 20 ppm.

#### Comparison Example 1

This catalyst was prepared using a commercially available silica gel where the sodium content was not reduced.

A commercial grade silica gel, "Davison "ID", manufactured by the Davison Chemical Division of W. R. Grace & Co., was used without further processing. A catalyst based on this material was prepared by following the method of Example 2 with the exception that the H<sub>2</sub>SO<sub>4</sub> treatment, which lowers sodium content, was not carried out. The resulting catalyst had a molybdenum loading of 9.7 wt.%, a sodium level of 520 ppm and a surface area of 282 m<sup>2</sup>/g (BET). This example, in effect, is what one would produce by following Example 1 of the Bayer German Offenlegungsschrift 2,404,738. There Bayer makes no reference to the need to limit sodium content and consequently it is likely that the silica used has a relatively high sodium level. Supporting this interpretation is the statement on page 4 of the publication that up to 5 wt.% Na<sub>2</sub>O may be present in the working catalyst.

- 13 -

#### Example 4

This example illustrates the preparation of a catalyst using an acid washed precipitated silica.

A 5 g sample of dry Davison Sylox-15 silica, which had previously been washed briefly at room temperature in dilute  $H_2SO_4$  at a pH of 3, was impregnated by incipient wetness with 1.08 g ammonium paramolybdate 4-hydrate dissolved in water. The resulting solid was calcined at 482°C for 3 hours, pressed together, washed and screened to US 25-35. The catalyst had a Mo loading of 9.9 wt. %, a sodium level of 310 ppm and a surface area of 164 m<sup>2</sup>/g (BET).

#### Example 5

This example illustrates the preparation of a catalyst using an acid washed silica gel having a lower Mo loading.

An acid washed silica gel catalyst was prepared according to the procedure in Example 3 except that the molybdenum loading was controlled to be only 1.8% Mo and the sodium level was reduced to 1 ppm.

#### Example 6

This example illustrates the preparation of a comparison catalyst using alumina as a support.

In a mixture of 31 g hydrogen peroxide (30%) and 379 cc water was dissolved 69.4 g ammonium paramolybdate 4-hydrate. The solution was then mulled into 500 g of an alumina made according to the procedure of U. S. Patent No. 4,154,812 and the paste extruded, dried overnight at 230°F, calcined for 3

- 14 -

hours at 900°F, crushed and screened to US 25-35. The catalyst had a Mo loading of 11.8 wt.%, a sodium level of 290 ppm and a surface area of 180 m<sup>2</sup>/g (BET).

#### Example 7

This example sets forth the evaluation of the catalysts made in Examples 1-6, Comparison Example 1, pure Cabosil, and the ultrapure support material made in Example 1 without any MoO<sub>3</sub>.

A 0.20 g (approx. 0.54 cc) sample of the screened catalyst was placed on a quartz frit in a 3/8" O.D. quartz tube and covered with 0.2 g US 25-35 screened quartz, which formed a preheating zone. A thermocouple was inserted into the bed such that its tip was at the entrance to the catalyst section.

Gas mixtures consisting of 95% methane and 5% oxygen and 90% methane and 10% oxygen, were passed through the tube at 1 atm, at gas hourly space velocities of 2500-10,000 hr<sup>-1</sup> (NTP) while the tube was heated to 575°, 600°, 625° and 650°C. The exit gases passed through heat traced Teflon<sup>(R)</sup> lines to a gas chromatograph where formaldehyde and carbon dioxide were analyzed in a Poropak T column in series with a methanizer and flame ionization detector. Other gases were analyzed using a thermal conductivity detector with a carbosphere column. The methanizer had been calibrated for formaldehyde against the chromatropic acid method. See West, P. W. and Sen B., Z. Anal. Chem. 153 (1956) 177-183. The results are set forth in Table 1. In this table oxygen consumption is defined



- 15 -

as the difference between the inlet and outlet oxygen concentrations at an operating pressure of 1 atm.

TABLE 1

| Examples                     | Description                                             | Mo%  | HCHO SELECTIVITIES AT DIFFERENT<br>VALUES OF O <sub>2</sub> CONSUMPTION |      |      |      |      |      |
|------------------------------|---------------------------------------------------------|------|-------------------------------------------------------------------------|------|------|------|------|------|
|                              |                                                         |      | 0.1%                                                                    | 0.2% | 0.5% | 1.0% | 2.4% | 3.2% |
| 1                            | MoO <sub>3</sub> Ultrapure Silica                       | 1.6% | 90                                                                      | 88   | 85   | 78   | 66   | 59   |
| 2                            | MoO <sub>3</sub> - Cabosil                              | 9.8  | 89                                                                      | 88   | 83   | 75   | 58   | 48   |
| 3                            | MoO <sub>3</sub> - Acid Washed<br>Silica Gel            | 8.6  | 74                                                                      | 73   | 68   | 63   | 52   | 49   |
| 4                            | MoO <sub>3</sub> - Acid Washed<br>Sylox 15              | 9.9  | 83                                                                      | 82   | 72   | 63   | 49   | 41   |
| 5                            | MoO <sub>3</sub> -Acid Washed<br>Silica Gel             | 1.8  | 96                                                                      | 89   | 81   | 71   | 59   | 55   |
| 6                            | MoO <sub>3</sub> - Alumina                              | 11.8 | 0                                                                       | 0    | 0    | 0    | 0    | 0    |
| Comparison<br>Ex. 1          | MoO <sub>3</sub> - Untreated<br>Silica Gel <sup>1</sup> | 9.7  | 67                                                                      | 66   | 59   | 42   | 27   | 23   |
|                              | Pure Cabosil                                            | 0    | 44                                                                      | 47   | 50   | 40   | 30   | 23   |
|                              | Ultrapure Silica                                        | 0    | --                                                                      | 40   | 31   | --   | --   | --   |
| Literature Values*           |                                                         |      |                                                                         |      |      |      |      |      |
| BAYER 2404738<br>Example 1   | MoO <sub>3</sub> - Silica                               | 10   | --                                                                      | --   | --   | --   | 33   | --   |
| U. S. 3,996,294<br>Example 1 | silica                                                  | 0    | --                                                                      | --   | --   | --   | --   | 38.1 |

\*Data reported in patent applications

<sup>1</sup> prepared according to BAYER 2404738

- 17 -

As the methane oxidation reaction continues to proceed further, as measured by the higher oxygen consumption, the selectivity to the formaldehyde intermediate decreases because more of the final end products of CO, CO<sub>2</sub> and H<sub>2</sub>O are formed. Within the range of conditions studied, the selectivity appeared to be a function of oxygen consumption, irrespective of the combination of temperatures and space velocities necessary to achieve this consumption.

The results show that the silica supported catalysts according to the present invention in Examples 1-5 are superior catalysts with selectivities as high as 96% whereas the alumina supported catalyst in Example 6 which does not contain silica is an unacceptable catalyst with no detectable formaldehyde synthesis activity.

Pure silica in the form of Cabosil showed some activity as an oxidation catalyst, but displayed a much lower selectivity to formaldehyde than the MoO<sub>3</sub> containing catalyst according to the present invention in Examples 1-5. Similarly just using ultrapure silica from Example 1 without any MoO<sub>3</sub> resulted in a poor catalyst with low selectivities.

Also presented in Table 1 were the two data points reported in Bayer German Offenlegungsschrift 2,404,738 (for 10 wt.% Mo and MoO<sub>3</sub> on SiO<sub>2</sub>) and in Imre et al. U. S. Patent 3,996,294 for pure silica. From reading the patents, there is no indication of the criticality of having a low sodium content. In Comparison Example 1 a MoO<sub>3</sub>-silica catalyst was made following these prior art teachings with a commercially available silica gel

- 18 -

where no attempt was made to reduce the sodium content. At each of the  $O_2$  consumption levels the selectivity of the catalyst of Comparison Example 1 is less than the levels obtained by using the low sodium catalyst according to the present invention.

The catalysts were also evaluated with a feed stream of 10%  $O_2$  in methane, at  $650^\circ C$ , at  $2500 \text{ hr}^{-1}$  (GHSV, NTP), and at 1 atm. The % methane conversion as determined by gas chromatography and the turnover number in micromoles methane converted per square meter of catalyst per hour (a measure of specific activity) are set forth in Table 2.

- 19 -

TABLE 2

| Examples            | Description                                  | BET  |                                      | CH <sub>4</sub><br>Conversion<br>% | Turnover Number<br>micromoles CH <sub>4</sub> converted<br>per m <sup>2</sup> catalyst per hour |
|---------------------|----------------------------------------------|------|--------------------------------------|------------------------------------|-------------------------------------------------------------------------------------------------|
|                     |                                              | Mo%  | Surface<br>Area<br>m <sup>2</sup> /g |                                    |                                                                                                 |
| 1                   | MoO <sub>3</sub> - Ultrapure Silica          | 1.6  | 47                                   | 5.9                                | 37.9                                                                                            |
| 2                   | MoO <sub>3</sub> - Cabosil                   | 9.8  | 210                                  | 4.3                                | 6.18                                                                                            |
| 3                   | MoO <sub>3</sub> - Acid Washed<br>Silica Gel | 8.6  | 232                                  | 6.1                                | 7.93                                                                                            |
| 4                   | MoO <sub>3</sub> - Acid Washed<br>Sylox 15   | 9.9  | 164                                  | 5.3                                | 9.75                                                                                            |
| 6                   | MoO <sub>3</sub> - Alumina                   | 11.8 | 180                                  | 5.5                                | 9.22                                                                                            |
| Comparison<br>Ex. 1 | MoO <sub>3</sub> - Untreated<br>Silica Gel   | 9.7  | 282                                  | 3.4                                | 3.64                                                                                            |
|                     | Pure Cabosil                                 | 0    | 312                                  | 2.2                                | 2.13                                                                                            |
|                     | Ultrapure Silica                             | 0    | 41                                   | 0.45                               | 3.31                                                                                            |

- 20 -

These results show that the ultrapure silica-supported molybdena catalyst has an exceptionally high specific activity. The molybdena-containing catalysts have activities which are higher than those of silica-only catalysts and the acid washed silica gel-supported molybdena catalyst has more than twice the specific activity of the "as received" silica gel-supported molybdena catalyst. The alumina-supported catalyst also has a high specific activity but as was set forth in Table 1, it produces no detectable formaldehyde and the methane is principally oxidized to carbon oxides and water.

#### Examples 8-11

These examples illustrate the effect of various concentrations of sodium on two types of silica supports.

Cabosil has less than 4 ppm Na and thus a sodium-loaded version was made by washing it in a dilute solution of sodium hydroxide having a pH of 10.2 at 100°C. Silica gel, on the other hand, contains substantial sodium as manufactured. Low-sodium versions were made by washing in dilute  $H_2SO_4$  having a pH of 3 at different temperatures. The supports were made into catalysts using the method of Example 2 for the treated and untreated Cabosil and the method of Example 3 for the treated and untreated silica gels. The catalysts were tested according to the procedure in Example 7 and the results are set forth in Table 3.

- 21 -

TABLE 3

| <u>Examples</u>  | <u>Description</u>                                   | <u>Mo%</u> | <u>Na (ppm)</u> | <u>HCHO selectivity<br/>at 2.4% O<sub>2</sub><br/>Consumption</u> |
|------------------|------------------------------------------------------|------------|-----------------|-------------------------------------------------------------------|
| 2                | MoO <sub>3</sub> - Cabosil                           | 9.8        | less than 4     | 58%                                                               |
| 8                | MoO <sub>3</sub> - Acid Washed (100°C)<br>Silica Gel | 8.6        | 20              | 52%                                                               |
| 9                | MoO <sub>3</sub> - Acid Washed (RT)<br>Silica Gel    | 9.8        | 300             | 39%                                                               |
| 10               | MoO <sub>3</sub> - Untreated Silica Gel              | 9.7        | 520             | 27%                                                               |
| 11               | MoO <sub>3</sub> - Na-Loaded Cabosil                 | 9.4        | 3600            | 8%                                                                |
| BAYER<br>2404738 | MoO <sub>3</sub> - Silica<br>(source unknown)        | 10         | unknown         | 33%                                                               |

- 22 -

Thus it can be observed that irrespective of the nature of the silica support, the presence of even small concentrations of sodium has a profoundly deleterious effect on the HCHO selectivity of methane oxidation when it is catalyzed by the  $\text{MoO}_3\text{-SiO}_2$  system.

#### Examples 12 and 13

These examples illustrate the efficiency of catalysts having low  $\text{MoO}_3$  loadings on silica for the partial oxidation of methane.

Acid washed silica gel catalysts were prepared according to the method set forth in Example 3, with the exception that the Mo loadings were 1.8 and 10%. The catalysts were tested according to the general procedure in Example 7 but at conditions of a GSHV of  $2500 \text{ hr}^{-1}$  at NTP, 1 atmosphere pressure, 10%  $\text{O}_2$  in  $\text{CH}_4$  and  $650^\circ\text{C}$ . The results are set forth in Table 4.



TABLE 4

SELECTIVITY TO HCHO AND ACTIVITY FOR METHANE OXIDATION<sup>1</sup> OF SiO<sub>2</sub>-MoO<sub>3</sub>  
BASED CATALYSTS AT SPACE VELOCITY OF 2500hr<sup>-1</sup> (GHSV, NTP) AND 650°C

| <u>Catalyst</u> | <u>Mo%</u> | <u>CH<sub>4</sub><br/>Conversion %</u> | <u>Selectivity<br/>to Formaldehyde</u> | <u>HCHO Yield<br/>(CH<sub>4</sub> basis)x10<sup>-4</sup></u> |
|-----------------|------------|----------------------------------------|----------------------------------------|--------------------------------------------------------------|
| Example 12      | 1.8        | 6.4                                    | 35%                                    | 224                                                          |
| Example 13      | 10         | 6.2                                    | 15%                                    | 93                                                           |

<sup>1</sup> Gas composition 10% O<sub>2</sub>, 90% CH<sub>4</sub>

- 24 -

The activity as measured by methane conversion and formaldehyde yield under identical conditions is higher for the catalyst containing the lower level of molybdenum of 1.8%. Yield is defined as the product of selectivity and conversion.

It is understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of this invention.

- 25 -

WHAT IS CLAIMED IS:

1. A process to make formaldehyde from methane comprising partially oxidizing methane with a molecular oxygen containing gas over a catalyst comprising  $\text{MoO}_3$  on a silica support having a low sodium content of less than 350 ppm, said amount of  $\text{MoO}_3$  being at least a catalytically effective amount and up to an amount where the Mo content is about 50% by weight of the catalyst.

2. A process according to Claim 1, wherein the support is a silica selected from the group consisting of silica obtained from the hydrolysis of silicon tetraalkoxides, fumed silica, acid washed silica gel, acid washed precipitated silica and mixtures thereof.

3. A process according to Claim 1, wherein the silica support has a BET nitrogen surface area of at least 20  $\text{m}^2/\text{g}$ .

4. A process according to Claim 1, wherein the silica support has a sodium content of less than 100 ppm.

5. A process according to Claim 4, wherein the silica support has a sodium content of less than 20 ppm.

6. A process according to Claim 5, wherein the silica support has a sodium content of about 1 ppm or less.

7. A process according to Claim 1, wherein the amount of  $\text{MoO}_3$ , expressed as wt% Mo, is an amount up to 15 wt% Mo.

8. A process according to Claim 7, wherein the amount of  $\text{MoO}_3$  is from about 0.5-15 wt% Mo.

9. A process according to Claim 2, wherein the silica is a silica obtained from the hydrolysis of silicon tetraalkoxides and the sodium content is less than 4 ppm.

- 26 -

10. A process according to Claim 9, wherein the sodium content is less than 2 ppm.

11. A process according to Claim 1, wherein the silica support is an acid washed silica gel.

12. A process according to Claim 1, wherein the silica support is an acid washed precipitated silica.

13. A catalyst suitable for the partial oxidation of methane comprising  $\text{MoO}_3$  on a silica support selected from the group consisting of acid washed silica gel, acid washed precipitated silica and mixtures thereof having a low sodium content of less than 350 ppm, said amount of  $\text{MoO}_3$  being at least a catalytically effective amount and up to an amount where the Mo content is about 50% by weight of the catalyst.

14. A catalyst according to Claim 13, wherein the silica support has a BET nitrogen surface area of at least  $20 \text{ m}^2/\text{g}$ .

15. A catalyst according to Claim 13, wherein the sodium content is less than 100 ppm.

16. A catalyst according to Claim 15 wherein the sodium content is less than 20 ppm.

17. A catalyst according to Claim 16, wherein the sodium content is about 1 ppm or less.

18. A catalyst according to Claim 13, wherein the amount of  $\text{MoO}_3$ , expressed as wt% Mo, is an amount up to 15 wt% Mo.

19. A catalyst according to Claim 18, wherein the amount of  $\text{MoO}_3$  is from about 0.5-15 wt% Mo.

20. A catalyst according to Claim 13, wherein the silica support is an acid washed silica gel.

- 27 -

21. A catalyst according to Claim 13, wherein the silica support is an acid washed precipitated silica.

22. A catalyst suitable for the partial oxidation of methane comprising  $\text{MoO}_3$  on a silica support having a silica purity of at least 99.99% silica, a total impurity level less than 100 ppm, and having a low sodium content of less than 50 ppm, said amount of  $\text{MoO}_3$  being at least a catalytically effective amount and up to an amount where the Mo content is about 50% by weight of the catalyst.

23. A catalyst according to Claim 22, wherein the silica support has a BET nitrogen surface area of at least  $20 \text{ m}^2/\text{g}$ .

24. A catalyst according to Claim 22, wherein the sodium content is less than 4 ppm.

25. A catalyst according to Claim 24, wherein the sodium content is less than 2 ppm.

26. A catalyst according to Claim 25, wherein the sodium content is 1 ppm or less.

27. A catalyst according to Claim 22, wherein the amount of  $\text{MoO}_3$ , expressed as wt% Mo, is an amount up to 15 wt% Mo.

28. A catalyst according to Claim 27, wherein the amount of  $\text{MoO}_3$  is from about 0.5-15 wt% Mo.

29. A catalyst according to Claim 22, wherein the silica is made by the hydrolysis of silicon tetraalkoxides.

## AMENDED CLAIMS

[received by the International Bureau on 16 July 1986 (16.07.86);  
original claim 29 cancelled; claims 13 and 22 amended; other claims unchanged (2 pages)]

10. A process according to Claim 9, wherein the sodium content is less than 2 ppm.

11. A process according to Claim 1, wherein the silica support is an acid washed silica gel.

12. A process according to Claim 1, wherein the silica support is an acid washed precipitated silica.

13. A catalyst suitable for the partial oxidation of methane comprising

a low sodium silica support selected from the group consisting of silica gel, precipitated silica, and mixtures thereof which has been made by the sustained washing of the silica with acid until the sodium content has been lowered to less than 350 ppm; and

MoO<sub>3</sub> on the acid washed support which is present in an amount from a catalytically effective amount for the partial oxidation of methane up to an amount where the Mo content is about 50% by weight of the catalyst.

14. A catalyst according to Claim 13, wherein the silica support has a BET nitrogen surface area of at least 20 m<sup>2</sup>/g.

15. A catalyst according to Claim 13, wherein the sodium content is less than 100 ppm.

16. A catalyst according to Claim 15, wherein the sodium content is less than 20 ppm.

17. A catalyst according to Claim 16, wherein the sodium content is about 1 ppm or less.

18. A catalyst according to Claim 13, wherein the amount of MoO<sub>3</sub>, expressed as wt% Mo, is an amount up to 15 wt% Mo.

19. A catalyst according to Claim 18, wherein the amount of MoO<sub>3</sub> is from about 0.5-15 wt% Mo.

20. A catalyst according to Claim 13, wherein the silica support is an acid washed silica gel.

21. A catalyst according to Claim 13, wherein the silica support is an acid washed precipitated silica.

22. A catalyst suitable for the partial oxidation of methane comprising  $\text{MoO}_3$  on a silica support made by the hydrolysis of silicon tetraalkoxides and having a silica purity of at least 99.99% silica, a total impurity level less than 100 ppm, and having a low sodium content of less than 50 ppm, said amount of  $\text{MoO}_3$  being at least a catalytically effective amount and up to an amount where the Mo content is about 50% by weight of the catalyst.

23. A catalyst according to Claim 22, wherein the silica support has a BET nitrogen surface area of at least  $20 \text{ m}^2/\text{g}$ .

24. A catalyst according to Claim 22, wherein the sodium content is less than 4 ppm.

25. A catalyst according to Claim 24, wherein the sodium content is less than 2 ppm.

26. A catalyst according to Claim 25, wherein the sodium content is 1 ppm or less.

27. A catalyst according to Claim 22, wherein the amount of  $\text{MoO}_3$ , expressed as wt% Mo, is an amount up to 15 wt% Mo.

28. A catalyst according to Claim 27, wherein the amount of  $\text{MoO}_3$  is from about 0.5-15 wt% Mo.

## STATEMENT UNDER ARTICLE 19

Claims 13 and 22 have been amended and Claim 29 cancelled. Pages 27 and 28 have been replaced with new pages 27 and 28 submitted herewith.

Claim 13 has been rewritten in terms of a low sodium silica support and the  $\text{MoO}_3$  on the support. Claim 13 specifies that the low sodium silica support has been made by the sustained washing of the silica with acid until the sodium content has been lowered to less than 350 ppm.

Claim 22 specifies that the silica support is made by the hydrolysis of silicon tetraalkoxides as was set forth in Claim 29 which has been cancelled.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US86/00474

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                |                                                                  |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------|
| <b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>3</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        |                                                                                                                |                                                                  |
| According to International Patent Classification (IPC) or to both National Classification and IPC<br><b>INT. Cl. 4</b> C07C 45/33; B01J 21/08; B01J 23/16<br><b>U.S. CL.</b> 568/482                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |                                                                                                                |                                                                  |
| <b>II. FIELDS SEARCHED</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                |                                                                  |
| Minimum Documentation Searched <sup>4</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            |                                                                                                                |                                                                  |
| Classification System                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | Classification Symbols                                                                                         |                                                                  |
| U.S.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | 502/482<br>568/482                                                                                             |                                                                  |
| Documentation Searched other than Minimum Documentation<br>to the extent that such Documents are included in the Fields Searched <sup>5</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                |                                                                  |
| W. R. Grace & Co.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                                                                                                |                                                                  |
| <b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |                                                                                                                |                                                                  |
| Category <sup>6</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup> | Relevant to Claim No. <sup>18</sup>                              |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | US, A, 2,102,160 (NASHA) 14 December 1937<br>See the claims                                                    | 1-12                                                             |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | US, A, 2,376,668 (DERBY) 22 May 1945<br>See the claims                                                         | 1-12                                                             |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | US, A, 2,625,519 (HARTIG) 13 June 1953<br>See the claims                                                       | 1-12                                                             |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | DT, A, 1,940,259 (KREISLER) 22 October 1970<br>See entire disclosure                                           | 1-12                                                             |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | UK, A, 1,244,001 (DOWDEN) 25 August 1971<br>See the claims                                                     | 1-12                                                             |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | UK, A, 1,398,385 (BUTCHER) 18 June 1975<br>See the claims                                                      | 1-12                                                             |
| A                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      | DT, A, 2,404,737 (IMRE) 21 August 1975<br>See the claims                                                       | 1-12                                                             |
| <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>16</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div> |                                                                                                                |                                                                  |
| <b>IV. CERTIFICATION</b>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |                                                                                                                |                                                                  |
| Date of the Actual Completion of the International Search <sup>3</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                                                                | Date of Mailing of this International Search Report <sup>3</sup> |
| 4 May 1986                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                | 23 JUN 1986                                                      |
| International Searching Authority <sup>1</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                         |                                                                                                                | Signature of Authorized Officer <sup>19</sup>                    |
| ISA/US                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |                                                                                                                | W. B. Lone                                                       |

| III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET) |                                                                                                                                                                        |                                    |
|----------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------|
| Category *                                                                 | Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>                                                         | Relevant to Claim No <sup>18</sup> |
| A                                                                          | DT, A, 2,404,738 (IMRE) 21 August 1975<br>See the claims                                                                                                               | 1-12                               |
| A                                                                          | US, A, 3,996,294 (IMRE) 07 December 1976<br>See abstract and claims                                                                                                    | 1-12                               |
| A                                                                          | US, A, 4,243,613 (BROCKHAUS) 06 January 1981<br>See abstracts and claims                                                                                               | 1-12                               |
| A                                                                          | JP, B, 0,092,629 (IWAMOTO) 02 June 1983<br>See the claims                                                                                                              | 1-12                               |
| A                                                                          | N, J. American Chemical Society, Vol. 106(15) Published 1984, (LIU),<br>"Partial Oxidation of Methane by Nitrous Oxide over Molybdenum on Silica. See pages 4117-4121, | 1-12                               |
| A                                                                          | N, J. Chemical Society, Chemical Communications Published 1982, (LIU),<br>"Partial Oxidation of Methane by Nitrous Oxide over Molybdenum on Silica. See pages 78-79    | 1-12                               |
| X                                                                          | US, A, 2,381,825 (LEE) 07 August 1945<br>See column 3, lines 1-3 and claims 1,2,4,5,7-9                                                                                | 13-20                              |
| X                                                                          | US, A, 4,284,369 (BERGNA ET AL) 08 November 1966. See Example 4 and claims                                                                                             | 13-20                              |
| A                                                                          | US, A, 4,280,929 (SHAW) 28 July 1981<br>See claims                                                                                                                     | 13-20                              |
| A                                                                          | US, A, 4,455,390 (TING) 19 June 1984<br>See claims                                                                                                                     | 13-20                              |

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE <sup>10</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers \_\_\_\_\_, because they relate to subject matter <sup>12</sup> not required to be searched by this Authority, namely:

2. ☐ Claim numbers \_\_\_\_\_, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out <sup>13</sup>, specifically:

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING <sup>11</sup>

This International Searching Authority found multiple inventions in this international application as follows:

I. Process for the preparation of formaldehyde: Claims 1-12

II. Catalyst suitable for oxidation: Claims 13-20

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

## Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.

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